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RP254

FURTHER STUDY OF PAPER-COATING MINERALS AND ADHESIVES

By Merle B. Shaw, George W. Bicking, and Martin J. O'Leary

ABSTRACT

Owing to the interest manifested among manufacturers in the investigation on Use of Glue in Coated Paper, Technologic Paper No. 323, other coating materials have recently been studied to keep the public informed of new developments in raw materials and promote the use of domestic resources. Four different clays, 2 foreign and 2 domestic, and 1 commercial compound of diatomaceous earth were the minerals employed. The domestic clays were from the same mine, but had received different refining treatment. One had been washed only; the other, chemically treated and washed. Three types of high-grade commercial adhesives—casein, glue, and modified starches—were used. The tests were confined to papers suitable for high-grade printing. The coating procedure was similar to commercial practice.

Present methods of refining American clay have improved its color, fineness, and suspension quality. The American clay that had been chemically treated and washed compared favorably in the tests with the foreign clays as paper-coating mineral. The coatings showed about the same differences in color as the clays themselves. The clay coatings were well bound to the fiber sheet and were of very good printing quality. The coating with the diatomaceous earth compound did not adhere well to the base paper.

It is doubtful whether the modified starches had quite as strong adhesive quality as the casein or glue, but all coatings containing 18 parts of starch per 100 parts of clay were well bound to the body papers. Graded as to their clay suspending property the adhesives were in the following descending order—starch, casein, and glue. There appeared to be no appreciable difference in the adhesives so far as their effect on the color of the coatings was concerned. When the coated papers were printed by the half-tone process equally good results were obtained with the three different adhesives, although the starch-bound coatings may possibly have absorbed somewhat more ink.

The publication includes chemical analyses, color measurements, and settling data for the minerals used, description of the coating procedure, and various measurements on the finished coated papers.

CONTENTS

I. INTRODUCTION AND RÉSUMÉ OF PREVIOUS WORK

The characteristic feature of mineral-coated papers is a thin layer of mineral matter and adhesive applied to the surface of the fiber sheet. The function of the mineral matter is to fill in the irregularities of the surface of the sheet to form a smoother and more even surface than that obtained by the other paper-manufacturing processes, while the adhesive is added to bind the particles of mineral matter together and to the body of the paper. There are many grades and uses of coated papers, and the coating materials employed are chosen according to the use for which the papers are intended. The tests described in the following pages, however, have been confined to papers for high-grade printing and lithographic purposes, for which a very even, semiabsorbent surface is required.

An investigation was previously made at the bureau to obtain data on the use of glue as adhesive in such types of coated paper. The work is fully described in Bureau of Standards Technologic Paper No. 323,[1] published in 1926. Consideration was given to the factors which materially influence the quality and price of the glue, and the printing quality of glue-bound coated papers. Eight different glues were used, with clays, satin white, and blanc fixe as the coating minerals.

Owing to the interest manifested by manufacturers in the previous work, other paper-coating materials have recently been studied to keep the public informed of new developments in raw materials and promote the use of domestic resources, which would become very important in the event of any disturbance limiting the supplies of foreign origin. The present paper describes these later tests, which are a continuation of the earlier work.

II. MATERIALS USED IN THE INVESTIGATION

1. PAPER

The base paper or body stock used for the coating tests was composed chiefly of sulphite pulp with some waste paper from experimental paper runs, and was medium rosin sized. The weight of the stock was approximately 54 pounds (500 sheets 25 by 40 inches in size). The paper was made on the Fourdrinier machine of the bureau's experimental paper mill, and was similar in its properties to that generally used in commercial coating mills.

The fibrous part of coated paper is sometimes regarded as a mere carrier of the coating and for this reason is sometimes very poor material. The quality of the body paper—its formation, cleanliness, color, and surface characteristics—is, however, of considerable importance. For good results in coating it is essential that the paper be well closed and the surface smooth and even. If it is too soft sized the coating mixture permeates too deeply and a poor bond between mineral and paper results. If it is too hard sized the coating will not adhere well to the surface. Freedom from surface dirt, specks, rosin, or lime spots, and other imperfections which may cause a local thinning or thickening of the coat is necessary to

[1] Use of Glue in Coated Paper, by George K. Hamill, V. H. Gottschalk, and George W. Bicking. Copies may be obtained from the Superintendent of Documents, Government Printing Office, Washington, D. C. Price 15 cents each.

insure uniform distribution of the coating on the body stock. The color of the base paper is a factor in the appearance of the coated sheet. The more nearly it corresponds to the color of the coating, the more satisfactory will be the results obtained.

2. COATING MATERIALS

(a) MINERALS

Four different coating clays—two foreign, two domestic—and a commercial compound of domestic diatomaceous earth,[2] designated herein as mineral No. 5, were the minerals employed. The foreign clays were graded as No. 1 and medium. The two domestic clays were from the same mine, but had received different refining treatment. One, clay A, had been washed only; the other, B, had been chemically treated, bleached, and washed. The following chemical analyses, color measurements, and settling data (Tables 1 to 3) give additional information on these materials.

Table 1.—*Chemical analyses of coating minerals* [1]

Constituents	Foreign clay		Domestic clay		Mineral No. 5
	No. 1	Medium	A	B	
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*
Silica (SiO_2)	46.7	46.2	44.4	44.3	28.4
Iron oxide (Fe_2O_3)	.7	1.0	.4	.4	.4
Alumina (Al_2O_3)[2]	37.5	37.6	39.8	41.0	.8
Calcium oxide (CaO)	Trace.	Trace.	Trace.	Trace.	47.6
Magnesium oxide (MgO)	.3	.5	.5	.1	.7
Loss at 110° C. (2 hours)	.4	.3	.6	.4	2.2
Further loss on ignition	12.4	12.5	13.7	14.0	20.0
Specific gravity at 15.6° C[3]	2.71	2.75	2.67	2.70	2.63

[1] Analyses made by chemistry division, Bureau of Standards.
[2] Includes TiO_2, P_2O_5, Mn_3O_4 if present.
[3] Specific gravity determined by A.S.T.M. method D 153-27.

Clays consist of finely divided mineral matter, chiefly silica and alumina, derived from rocks by disintegration. They may be either residual or transported. The residual (or primary) clays are those which remain overlying the rocks from which they have been formed, and they are thus distinguished from transported (sedimentary or secondary) clays, which have been carried from their place of origin by eroding influences and redeposited. Because of the largeness of the deposits and their residual character, foreign clays are in their natural state considered homogeneous. The majority of American clays are transported and, therefore, may contain more impurities. For this reason more attention in refining is needed for the American clays, but by modern improved methods of handling and purification, the extraneous substances are reduced to a satisfactory minimum, and the American clays now available are greatly improved.

As shown in the chemical analyses of Table 1, the domestic clays tested were similar to the foreign clays in composition. Mineral No. 5 had a very high lime content. The low moisture content of the

[2] Fine powder obtained from the accumulated deposits of diatoms, microscopic unicellular algæ remarkable for their silicified cell walls, which persist after the death of the organism.

clays, "loss at 110° C.," was doubtless due to the fact that they had been kept in a dry place for a considerable time before the tests. Under "further loss on ignition" is given the loss chiefly of chemically combined water and organic matter.

The color or degree of whiteness is important in the selection of minerals for use in high-grade papers. A Pfund colorimeter [3], which gives numerical values as a basis for comparison, was used to determine the color characteristics reported in Table 2 and shown graphically in Figure 1. Magnesium oxide was included with the samples in order to give a value of white for comparative purposes.

TABLE 2.—*Color measurements of coating minerals* [1]

	Brightness values		
	Blue (wave length 460 mμ)	Green (wave length 550 mμ)	Red (wave length 625 mμ)
Magnesium oxide [2]	0.871	0.928	0.937
Foreign clay No. 1	.791	.850	.870
Foreign clay medium	.750	.812	.834
Domestic clay A	.753	.838	.876
Domestic clay B	.807	.901	.922
Mineral No. 5	.763	.834	.869

[1] Measurements made by R. E. Lofton, Bureau of Standards.
[2] Magnesium oxide was included for comparison.

The color characteristics are shown in terms of the relative brightness of the three primary components—blue, green, and red. If the sample being tested were truly color neutral, "white" or gray, it would reflect nonselectively and the brightness values for the three colors would be the same. The color curve would be a straight, horizontal line, but since white has a higher brightness value than gray the curve for white would be higher on the vertical scale. As the color becomes more selective; that is, shows a tint or dominant hue, the values for the reflection coefficient diverge.

As shown in Figure 1 the domestic clays are somewhat more deficient in blue (that is, are more yellowish) than the foreign clays, but higher in brightness. The refining treatment given clay B improved its color characteristics. If a small amount of blue dye were added with the clay, it would doubtless be as good in color as the foreign clays. Its color curve would then be more nearly horizontal, but the brightness values would be somewhat lower.

The relative rates of settling from water suspensions are shown for the different clays in Table 3 and Figure 2. Using a water-clay ratio of 19.6 to 1, 200 ml of clay slip (clay content, 10 g) was placed in a graduated glass cylinder and the volume of clear supernatant liquid determined at various times. No electrolyte was added to deflocculate the clays.

The curves of Figure 2 afford a fairly accurate comparison of the fineness of the clay particles. The washing and chemical treatment of clay B apparently removed some of the coarse particles. It may

[3] Pfund, A. H., A New Colorimeter for White Pigments and Some Results Obtained by Its Use, Am. Soc. for Test. Matrls.; June, 1920.

possibly also have developed some colloidal property which increased the suspending quality of the clay. Whereas domestic clay A settled comparatively rapidly, the settling rate and final volume of wet clay were practically the same for domestic clay B as for the foreign clays. Fineness of grain and good suspension quality are essential to a free-flowing coating slip that will spread well on the paper and have good covering power. It is believed a clay of fine particle size will also take a better finish.

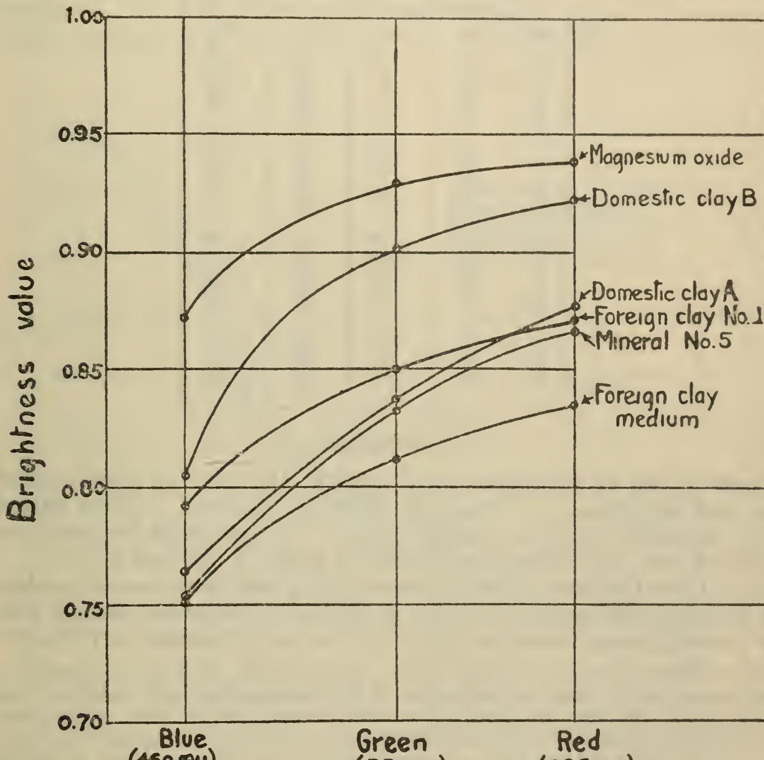

FIGURE 1.—*Color characteristics of coating minerals*

The water used for the slips had a pH value of 6.9, which is practically neutral. The pH of the clear liquid above the clay suspensions was 7.1 for foreign clay No. 1, 6.7 for foreign clay medium, 5.5 for domestic clay A, and 6.0 for domestic clay B; that is, the foreign clays were nearly neutral, whereas the domestic clays were somewhat acid in character. The corresponding value for the diatomaceous earth compound was 8.4.

TABLE 3.—*Rate of settling of clay in water*

$\left(200 \text{ ml of clay slip; } \frac{W}{C} = \frac{19.6}{1}\right)$

Time interval	Clear liquid above clay suspension			
	Foreign clay		Domestic clay	
	No. 1	Medium	A	B
Hr. Min.	*ml*	*ml*	*ml*	*ml*
0 0	0	0	0	0
0 10	13	7	77	14
0 20	30	27	133	27
0 30	53	47	145	40
0 40	82	68	149	52
0 50	99	86	151	65
1 00	109	103	153	76
1 15	115	112	155	90
1 30	120	116	157	105
1 45	123	119	158	120
2 00	126	122	159	132
2 30	132	126	162	138
3 00	136	130	165	142
3 30	139	134	166	144
4 00	142	137	167	146
5 00	147	142	168	150
6 00	152	146	169	153
7 00	155	150	170	155
24 00	162	160	171	164

(b) ADHESIVES

Three types of adhesives were used in the coating work—casein, glue, and modified, or chemically treated, starches. Three samples of the modified starches, called "gums" by the manufacturer, were employed and are designated herein as gums A, B, and C.

All of the adhesives employed were high-grade commercial products. The glue was the same as the No. 4 adhesive used in the earlier work.[4] The coating gums were described by the manufacturer as follows:

> These coating gums were made from cornstarch by chemical processes consisting essentially of weak esterification at low temperature with relatively weak organic acids, yielding products which tend toward slight acidic hydrolysis in the course of drying of the films. During the course of manufacture the starches were treated with soluble silicates, so that during the acidic hydrolysis the silicates are converted into silica gel in situ, and there is produced during the drying of the adhesive in contact with the clay coat, a combination of starch and silica gel. The silica gel assists in the bonding of the starch and clay and renders the coat somewhat more resistant to the leaching effects of water than is obtainable with the ordinary types of soluble starches previously used for such purposes.

All of the adhesives possessed the qualities given in Technologic Paper No. 323 as desired in adhesives for coating purposes, namely:

> Minimum of insoluble matter, such viscosity as to permit the use of ordinary equipment at the desired dilution of the coating mixture and within the temperature range of working conditions, high adhesiveness, good clay-suspending power, minimum of foam-causing impurities and grease.

III. EQUIPMENT USED

The paper mill of the bureau is equipped for coating paper on a semicommercial scale under practical mill conditions. The equipment

[4] B. S. Tech. Paper No. 323, p. 647.

employed consists of a 14-inch Waldron flat-bed brush coater with festoon dryer and rewinder, mixing tanks with power-driven agitators of the wooden-gate type, and a 5-roll supercalender.

The coating machine is the "single" coater type, applying the coating substance to but one side of the paper. It has 6 brushes, 2 rotating and 4 having a laterally reciprocating movement, to spread and smooth the coating material. The brushes, the first of which consists of comparatively coarse bristles and the last of fine, are placed in the following order: One rotating which applies the coating substance, one working across the surface of the paper with a reciprocating motion, another rotating, and three more reciprocating, the

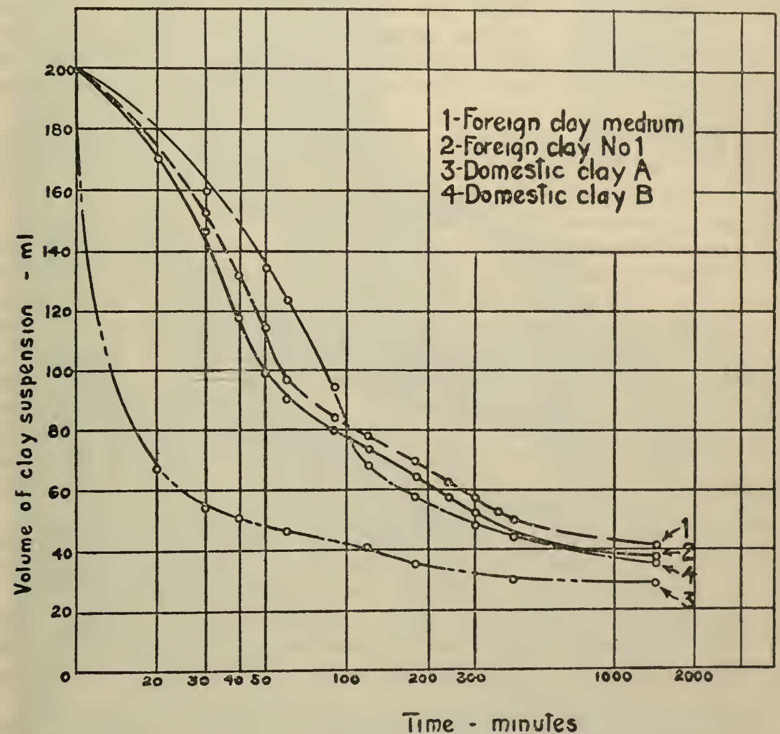

FIGURE 2.—*Rate of settling of clay in water* $\left(\frac{W}{C}=\frac{19.6}{1}\right)$

last having very fine badger bristles to eliminate any remaining marks made by the coarser ones. The pressure of the brushes on the paper can be adjusted so as to distribute the coating materials uniformly and smoothly over the paper.

The festoon rack is 15 feet long and has a capacity of 28 loops, each 6 feet in length. With the uptake rack and the rack from the festoons to the reel, the capacity of the dryer is approximately 400 lineal feet. The dryer is inclosed in a cabinet equipped for air conditioning and temperature control. The photograph of Figure 3, however, was made before the cabinet was installed.

The mixing tanks used for preparing the coating mixtures are shown in Figure 4.

The supercalender (fig. 5) is equipped to calender paper either in the web or in sheets. The drive is such that the calender can be run at almost any speed desired. The lever-weight arms are raised or lowered hydraulically. The calender is supplied with 3 steel and 3 cotton rolls, so that the rolls can be alternated or the 3 cotton rolls can be used together.

IV. COATING PROCEDURE

1. PREPARATION OF COATING MIXTURE

The clay used in the coating mixtures was soaked in water overnight in order that it might become thoroughly wet before the slip was prepared. The slip was agitated for approximately one hour, after which the adhesive was added. The resultant coating mixture was agitated until uniform, the time required being from one to two hours.

The adhesive materials were added in solution. The casein and glue formulas developed and adopted in the earlier work and the formula recommended for the gums by the manufacturer were followed in the tests on the respective materials.

The casein was soaked for one hour at room temperature in approximately four times its weight of water and was occasionally stirred meanwhile. Since casein is insoluble in water, it was brought into solution by adding alkali solvents and heating the mixture to 130° to 150° F. The solution was allowed to cool to room temperature before it was added to the clay slip. Soda ash is probably the best solvent, or cutting alkali, for casein, but small amounts of borax, ammonia, and trisodium phosphate (alone or in combination) are used by mills with very satisfactory results. Nearly every manufacturer has a formula of his own, largely determined by the mill's coating process and the requirements of its customers.

The glue was soaked in water overnight and subsequently warmed to not more than 135° F. for solution. The solution was allowed to cool to room temperature before it was added to the clay slip.

The gums were mixed with water, heated at 185° to 190° F. until the solution was amber in color, and, as recommended by the manufacturer, added while hot to the clay slip, which was at room temperature.

After being screened through a No. 200 sieve the coating mixtures were ready to be applied to the body paper. The small scale coating equipment employed did not permit using the relatively high concentration used with commercial equipment, therefore, the mixtures were of lower concentration and the coatings obtained were consequently of comparatively light weight.

2. COATING

The coating procedure was similar to the commercial practice used in applying a single coating to paper. A roll revolving in the prepared coating mixture transferred the coating substance to a revolving brush, which, in turn, applied it to the surface of the paper. By means of the series of brushes pressing against the paper as it passed over the flat bed of the machine, the mixture was immediately smoothed out and brought into good contact with the paper. After leaving the brushes the paper was hung in a series of festoons or loops and

FIGURE 3.—*Paper coating machine (without drying cabinet)*

Paper shown festooned for drying.

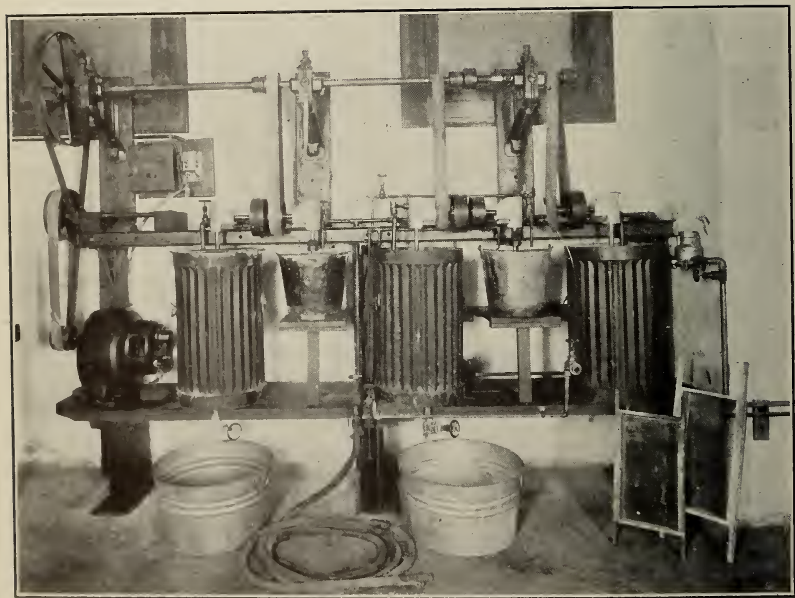

FIGURE 4.—*Mixing vessels*

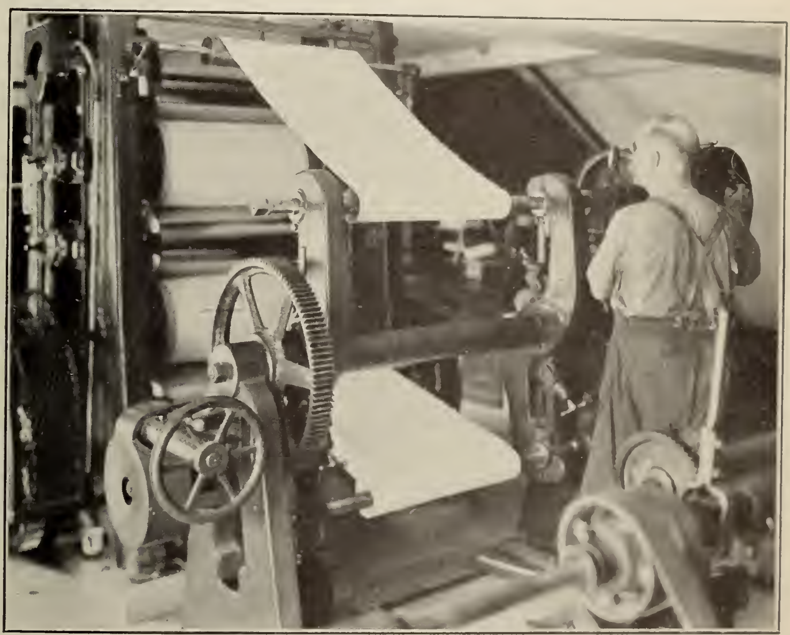

FIGURE 5.—*Supercalender*

carried along on an overhead trackway through the drying gallery, heated by hot air rising from near the floor, and then reeled up ready for calendering.

In order to sufficiently dry the coated paper in the short time required for it to pass through the cabinet, it was necessary to shut off the humidifying feature of the equipment. The moisture content of the paper entering the cabinet was approximately 35 per cent, and the interval permitted for drying was about 10 minutes (for 400 feet). If the paper admitted had been low in moisture content or could have been left longer to become dry and conditioned, the automatic humidity control would have been used. The temperature of the drying cabinet was from 110° to 120° F., but the paper was kept comparatively cool by the rapid evaporation caused by the large volume of warm air circulated from beneath.

3. CALENDERING

A combination of alternate steel and cotton rolls was used in calendering the paper, which was passed through in the web. No attempt was made to obtain a high glossy finish, the smoothness imparted by light calendering being sufficient for high-grade printing except for special cases.

V. TEST RESULTS

1. COATING OF PAPER

(a) MINERALS

The clays worked satisfactorily with the different adhesives. No attempt was made, however, to determine the minimum amount of each adhesive that could be used with them. The suspension quality of the clays was good, the coating mixtures screened satisfactorily, and the slips were spread without difficulty by the coating machine. Nearly any finish desired could have been obtained in the calendering but 70 per cent gloss [5] was the finish arbitrarily adopted.

The measurements on the coated papers are given in Table 4.

[5] The gloss of the finished papers was determined according to the Paper Testing Methods published by the Technical Association of the Pulp and Paper Industry, 18 East Forty-first Street, New York, N. Y.

TABLE 4.—*Coating mixtures and measurements on the finished coated papers* [1]

Run No.	Coating mixture: Mineral: Kind	Coating mixture: Mineral: Amount	Coating mixture: Water added to mineral	Coating mixture: Adhesive: Kind	Coating mixture: Adhesive: Amount	Coating mixture: Water added to adhesive	Coating mixture: Ratio of water to solids [2]	Coating mixture: Density [3]	Coated paper: Weight (25 by 40 inches, 500 sheets): Body stock	Coated paper: Weight (25 by 40 inches, 500 sheets): Coated paper	Coated paper: Color measurements (Brightness values): Blue (wave length 460 mμ)	Coated paper: Color measurements (Brightness values): Green (wave length 550 mμ)	Coated paper: Color measurements (Brightness values): Red (wave length 625 mμ)	Coated paper: Color measurements (Brightness values): White [4]	Coated paper: Gloss
		g	*g*		*g*	*g*		*Sp. gr. °F.*	*Pounds*	*Pounds*					*Per cent*
133	Foreign clay No. 1	2,000	2,500	Casein	350	1,500	1.9–1	1.24 at 77	54.2	68.2	0.769	0.864	0.912	0.867	66.7
134	do	2,000	2,500	do	350	1,500	1.9–1	1.24 at 76	54.2	67.6	.778	.871	.923	.878	66.7
143	do	2,000	2,500	Glue	250	2,000	2.0–1	1.24 at 81	54.2	65.4	.765	.858	.907	.868	74.6
149	do	2,000	3,000	Gum A	480	1,500	2.2–1	1.20 at 80	54.2	68.4	.756	.854	.914	.872	64.8
151	do	2,000	3,000	Gum B	480	1,500	2.0–1	1.25 at 89	54.2	73.4	.755	.853	.909	.870	72.9
152A	do	2,000	3,000	do	360	1,500	2.1–1	1.23 at 89	54.2	66.2	.767	.858	.908	.873	69.7
152B	do	2,000	3,000	do	360	1,500	2.4–1	1.20 at 80	54.2	62.6	.762	.853	.913	.874	70.5
153A	do	2,000	3,000	do	240	1,000	1.8–1	1.27 at 88	54.2	70.1	.783	.861	.920	.881	76.4
153B	do	2,000	3,000	do	240	1,000	2.2–1	1.22 at 88	54.2	63.6	.786	.864	.922	.878	69.5
135	Foreign clay medium	2,000	2,500	Casein	350	1,500	1.9–1	1.25 at 76	54.2	63.5	.756	.858	.906	.863	67.7
136	do	2,000	2,500	do	350	1,500	1.9–1	1.25 at 78	54.2	70.9	.751	.857	.899	.865	72.9
137	do	2,000	2,500	do	350	1,500	1.9–1	1.24 at 82	54.2	68.9	.747	.850	.898	.858	69.7
144	do	2,000	2,500	Glue	250	2,000	2.0–1	1.24 at 83	54.2	65.5	.741	.848	.896	.853	74.8
138	Domestic clay A	2,000	2,500	Casein	350	1,500	1.9–1	1.25 at 77	54.2	72.3	.752	.867	.913	.869	72.2
139	do	2,000	2,500	do	350	1,500	1.9–1	1.24 at 80	54.2	70.3	.742	.853	.907	.862	71.7
142	do	2,000	2,500	do	350	1,500	1.9–1	1.24 at 80	54.2	67.3	.741	.858	.912	.870	71.7
156	do	2,000	3,000	do	350	2,000	2.3–1	1.20 at 87	54.2	62.3	.763	.861	.924	.878	69.0
145	do	2,000	2,500	Glue	250	2,000	2.0–1	1.24 at 82	54.2	65.2	.743	.850	.900	.865	77.7
147	do	2,000	3,000	do	250	2,500	2.4–1	1.20 at 83	54.2	63.5	.742	.850	.908	.864	75.2
148A	do	2,000	3,000	do	250	2,000	2.2–1	1.22 at 82	54.2	68.2	.752	.852	.917	.874	66.7
148B	do	2,000	3,000	do	250	2,000	2.4–1	1.20 at 82	54.2	63.8	.747	.855	.916	.868	69.2
155	do	2,000	3,000	do	250	1,000	2.4–1	1.20 at 84	54.2	62.6	.755	.863	.924	.880	74.8
150A	do	2,000	3,000	Gum A	480	1,500	2.4–1	1.23 at 85	54.2	68.7	.732	.848	.912	.870	64.3
150B	do	2,000	3,000	do	480	1,500	2.4–1	1.23 at 85	54.2	61.9	.747	.855	.918	.871	64.0
150C	do	2,000	3,000	do	480	1,500	2.6–1	1.19 at 80	54.2	61.6	.742	.850	.914	.868	61.6
154	do	2,000	3,000	do	360	1,500	2.3–1	1.21 at 84	54.2	66.2	.728	.850	.912	.875	71.0
157	do	2,000	3,000	do	360	1,500	2.3–1	1.22 at 88	[5] 52.9	65.6	.682	.773	.827	.790	68.5

159	Domestic clay B	2,000	3,000	Casein	350	1,500	2.3–1	1.21 at 80	[5] 52.9	66.0	.685	.769	.822	.787	70.0
165	do	2,000	3,000	do	300	1,500	2.3–1	1.21 at 80	[5] 52.9	66.0	.671	.756	.815	.778	71.2
158	do	2,000	3,000	Glue	250	2,000	2.4–1	1.20 at 80	[5] 52.9	63.4	.672	.755	.810	.768	71.2
160	do	2,000	3,000	do	250	2,000	2.4–1	1.22 at 80	[5] 52.9	67.4	.688	.767	.820	.777	71.5
161	do	4,000	7,000	Gum B	720	3,000	2.3–1	1.22 at 80	[5] 52.9	69.1	.671	.761	.813	.769	76.6
163	do	2,000	3,000	do	360	2,000	2.3–1	1.21 at 80	[5] 52.9	70.0	.675	.766	.812	.785	72.4
164	do	2,000	2,500	do	360	3,000	2.5–1	1.20 at 84	[5] 52.9	66.1	.665	.752	.808	.767	69.5
166	do	2,000	3,500	do	360	2,000	2.3–1	1.22 at 85	[5] 52.9	66.1	.670	758	.820	.785	69.5
162	do	4,000	7,000	Gum C	720	3,000	2.1–1	1.23 at 80	[5] 52.9	69.5	.672	.754	.808	.768	76.2
	Mineral No. 5 [6]														

[1] Color and gloss measurements made by W. L. Holt, Bureau of Standards.
[2] Solids include coating mineral, adhesive, and chemicals used in the coating mixture.
[3] Specific gravity determined by hydrometer method.
[4] Measurements made without color filter.
[5] Body stock for these tests different from that for the preceding.
[6] Results obtained with mineral No. 5 were unsatisfactory, as shown in text, therefore, measurement on the papers coated with this mineral were not made.

As indicated in the table the coatings showed about the same differences in color as the clays themselves; that is, the coated paper for which domestic clay B was used was somewhat better in color than that coated with sample A, and compared favorably with the color of the papers coated with the foreign clays. There appears to be no appreciable difference in the adhesives so far as their effect on the color of the coatings is concerned. Since starch is comparatively a very white material it might be expected to affect the color least, with casein and glue following in order, but these differences were not shown in the measurements. The weight of the single coat applied was approximately from 10 to 15 pounds on a basis paper 25 by 40 inches, 500 sheets.

Mineral No. 5 is primarily a ceramic material, but because of its softness and fineness was thought to be a possible coating mineral. Casein and glue were used as the adhesives in the coating tests. When the casein mixture was added to the slip of mineral and water the resultant mixture was very fluid, whereas when the glue solution was added to the mineral slip the mixture was very thick and plastic. The coating did not hold well; that is, could be easily picked off. It was thought that the loss of binding quality of the adhesive was caused by the alkalinity of the mineral matter. (The chemical analysis, p. 1191, shows the lime content of the mineral to be very high.

It was thought that the addition of alum might give a product having some of the characteristics of satin white (a prepared compound of aluminum sulphate and lime used as coating material), therefore, preliminary tests were made to determine the amount of alum required to neutralize the alkalinity of the mineral. For 100 g of mineral 200 g of alum was needed to make the mixture neutral. Coating runs were made, but the binding quality of the coat was still unsatisfactory.

It is believed that mineral No. 5 is unsatisfactory for use as a coating material when casein or glue is used as adhesive and handled in accordance with the usual coating procedure. There is a possibility that with a special adhesive, one that could be employed when considerable alkali (lime) is present, it might be suitable for coating use.

The color of mineral No. 5 is not so good as most grades of coating clays. The greater cost of the material as compared with good grades of clay would also doubtless be a deciding factor in its use for paper coating.

(b) ADHESIVES

The amount of casein employed was, except in one case, 17.5 per cent, and of glue 12.5 per cent, based on the weight of the mineral being used. The results attributable to these materials were very satisfactory, and duplicated those previously obtained. (Tech. Paper No. 323.)

In the work with the starches two different proportions of gum A, 24 and 18 per cent, based on the clay content, were employed. No trouble was experienced in the tests (runs Nos. 149, 150, 154, and 157) and the adhesive quality of the gum, as judged by the sealing wax pick test,[6] which approximates the sort of surface pull received by the paper in the printing operation, was satisfactory.

[6] The end of a stick of sealing wax is softened by warming and then applied with firm pressure to the coating. With the paper held down firmly on either side of the wax, the stick is drawn away from the paper by a steady vertical pull. If fibers from the body stock adhere to the wax, it is an indication that the coating is firmly bound and should not pick off in the printing process. The test is comparative only, and requires that the area of contact between wax and paper be the same for all samples to be compared.

In the first series of runs with gum B (Nos. 151 to 153) 24, 18, and 12 per cent of gum, respectively, were used. There seemed to be a tendency for the gum solutions to jell after being added to the clay slip. Small jell particles remained in the coating mixture even after it had been screened through a No. 200 sieve. Spots of localized variations in thickness and translucency ("bird's-eyes") were noted in the coated papers and were thought probably to have been caused by the jell particles. Graded in regard to the degree of adhesion of the coating to the body stock, the papers were in the same relative order as the amounts of gum used.

A greater quantity of water was used in preparing the gum mixture for the next runs with gum B. Whereas the ratio had been 1 part of gum to 4 parts of water in the previous runs, for runs Nos. 163 and 164, 6 and 8 parts of water, respectively, were used. It was believed that the greater dilution might prevent the formation of jell particles, but the coating was no better than that obtained when 4 parts of water were used.

In the belief that the chemical preparation of the gum might be such that when the mixture is agitated a comparatively long time the jell develops in the slip rather than on the paper during the coating and drying processes, the coating mixture for the next run (No. 168) was agitated for a shorter time, and the interval between the adding of the gum to the clay slip and the application of the coat to the paper was briefer. There was no formation of jell in the coating mixture before it was applied to the paper, and none of the trouble experienced in the previous tests was encountered.[7]

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[7] Since the tests were made it has been found that the tendency for the gum to jell during the agitation of the clay mixture can be eliminated also by increasing the hydroxyl ion concentration of the coating mixture. Reports to the bureau of subsequent commercial mill tests stated the following:

"In light of the experience gained at the Bureau of Standards, where the pH of the coating mixture was approximately 8, it was found desirable in commercial mill tests to cook the gum at a higher pH or basicity. In the commercial runs one-half per cent, based on the weight of gum, of 26° Bé. ammonia was added to the water in which the gum was to be cooked, and the gum was thoroughly stirred in the water before the direct steam was admitted for cooking. The heating was either continued for a longer period or at a slightly higher temperature (approximately 195° to 205° F.) than was used at the Bureau of Standards. It was found preferable to judge the completion of the cooking by the color reaction of the gum, which was a deep amber when the cooking was completed. It is believed that the gum has better binding quality when handled this way.

"Further commercial experience showed that it is preferable to add from one-fourth to one-half per cent, based on the clay, of 26° Bé. ammonia to the water in which the clay is stirred, as this makes an improvement in the final coating mixture, in addition to helping to smooth down the clay. When the hot gum solution is added the pH of the resulting coating mixture is approximately 10.

"Operating on the above basis, the formula for commercial runs would be as follows:

Clay slip	Gum
100 pounds clay. 75 pounds water. One-fourth to one-half pound 26° Bé. ammonia.	18 pounds gum. 72 pounds water. 2 to 3 ounces 26° Bé. ammonia.

"Coating gums B and C have been successfully used commercially in coating also with mixtures of clay and satin white. Due to the fine state of subdivision of satin white and to its somewhat alkaline reaction a larger percentage of gum C should probably be used, depending upon the amount of satin white admixed with the clay. Unlike the procedure with casein as the adhesive, the clay satin-white slip should be at a fairly high temperature when the coating gum is added, as this provides the lower viscosity and a better spreading mixture.

"A typical formula for work with satin-white mixtures is as follows:

Clay satin-white slip	Gum
75 to 100 pounds water. 100 pounds clay. 200 pounds satin white.	228 pounds water. One-fourth pound ammonia (26° Bé.). 57 pounds coating gum.

Stir the clay satin-white mixture for two hours or until perfectly smooth and then add the solution of coating gum. To prepare the gum solution stir cold until gum is dispersed evenly, then apply heat by direct steam until 190° to 195° F. is reached, maintaining this or a slightly higher temperature for a sufficiently long period to produce a clear amber-colored solution. Cool the gum solution to 140° to 160° F. and add to the clay satin-white slip, stirring continually meanwhile. Then adjust the coating mixture to the necessary concentration and fluidity for application on the coating machine."

Gum C was used for run No. 162. The coating was very satisfactory.

The relative effect of the adhesive on the suitability of the coated papers for writing was shown in a general way by writing on the papers with a pen and ordinary blue-black ink and noting the ease with which the operation was effected and the definition of the lines. In each case the quality of the writing was satisfactory, but the casein-bound coatings offered the least resistance to the mechanical action of the pen, the effort required in execution being greatest where starch was the adhesive employed.

2. PRINTING TESTS

Printing tests were made at the Government Printing Office on the coated papers. The cooperation of the Government Printing Office in making the tests, which were an important part of the investigation, is gratefully acknowledged.

The experimental coated papers were substituted for the regular stock being printed by the half-tone process. No changes were made in the printing machine or the inks. The tests showed the coatings to be well bound to the body paper and of very good printing quality. Equally good results were obtained with the American and foreign clays and with the three different kinds of adhesives, although the starch-bound coatings may possibly have absorbed somewhat more ink. Both starch and glue coatings have generally been found to have less water resistance than casein coatings and, therefore, may possibly not be suitable for lithographic processes requiring a high degree of water resistance.[8]

VI. CONCLUSIONS

The tests indicate the following general conclusions relative to the materials studied.

1. Present methods of refining American clay have improved its color, fineness, and suspension quality. American clay that had been washed and chemically treated compared favorably with foreign clays as paper-coating mineral. Diatomaceous earth compounds having a large lime content are not satisfactory when the coating mixtures are prepared by the usual procedure.

2. Graded as to their clay-suspending property, the adhesives used are in the following descending order—starch, casein, and glue. Graded as to the suitability of the coatings for ink writing the apparent order is casein, glue, and starch.

3. Starch coating mixtures are not as free-flowing as mixtures in which casein or glue are used as the adhesive, but the starch mixtures used in the tests spread and brushed out satisfactorily.

4. It is doubtful whether modified starch has quite as strong adhesive quality as casein or glue, but all sheets of the foregoing tests containing 18 parts of starch per 100 parts of clay were entirely satisfactory in this respect, judged by either the sealing wax pick test or the printing experiments. Results reported for subsequent commercial tests were in agreement with those obtained at the bureau.[9]

[8] Reports on a variety of commercial printing tests indicate, however, that "the gum-bound coating does not readily leach off, and this feature seems to explain its adaptability to most lithographic work."

[9] Commercial printing tests on the commercially coated papers (footnote 7, p. 1201) were reported as satisfactory even for the papers for which 15 per cent of gum had been used, "even for multicolor work using tacky inks, including the tackiest solid black."

5. The surface of starch-bound coated papers appears to be more absorbent than that of papers for which glue or casein is used as adhesive for the mineral, and consequently ink may penetrate it to a greater extent. For this reason it might be expected that printings on the starch-bound coatings would tend to be blurred unless special care was used in the operation, but this tendency was not apparent in the printing tests on the experimental papers.

The manufacturer of some coated papers may wish to use casein in order to give his paper good printing quality regardless of whether the paper is dampened. A high degree of water resistance is not required for a large majority of printing papers, such as book, magazine, and catalogue, however, and starch-coated papers could apparently be used for these very satisfactorily.

6. Notwithstanding its lack of water resistance, modified starch has a number of attractive qualities. It is clean, does not have an unpleasant odor, and is cheap. When comparing the price of casein with that for glue or starch, the cost of solvents for the casein must also be taken into consideration, although in the case of starch, the greater percentage required reduces the cost differential somewhat.

WASHINGTON, September 30, 1930.

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